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Poling-assisted bleaching of soda-lime float glasses containing silver nanoparticles with a decreasing filling factor across the depth

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The recently discovered poling-assisted bleaching of glass with embedded silver nanoparticles has renewed the interest in thermal poling as a simple, reliable, and low-cost technique for controlling locally the surface-plasmon-resonant optical properties of metal-doped nanocomposite glasses. In the present study, the emphasis is put on the influence of the volume filling factor of metallic clusters on poling-assisted bleaching. Soda-lime silicate glass samples containing spherical silver nanoparticles with a decreasing filling factor across the depth were subject to thermal poling experiments with various poling temperatures, voltages, and times. Optical extinction spectra were measured from ultraviolet to near-infrared ranges and the surface-plasmon-resonant extinction due to silver nanoparticles (around 410 nm) was modeled by the Maxwell Garnett [Philos. Trans. R. Soc. London, Ser. A **203**, 385 (1904); **205**, 237 (1906)] effective medium theory which was adapted in order to take into account the filling factor depth profile. A method was proposed for the retrieval of the filling factor depth profile from optical extinction spectra recorded in fresh and chemically etched samples. A stretched exponential depth profile turned out to be necessary in order to model samples having a high filling factor near the surface. Based on the fact that the electric-field-assisted dissolution of embedded metallic nanoparticles proceeded progressively from the top surface, a bleaching front was defined that moved forward in depth as time elapsed. The position of the bleaching front was determined after each poling experiment by fitting the measured extinction spectrum to the theoretical one. In samples with higher peak value and steeper gradient of the filling factor, the bleaching front reached more rapidly a steady-state depth as poling time increased. Also it increased less strongly with increasing poling voltage. These results were in agreement with the physics of the dissolution process. Finally, clear evidence of injection of hydrogenated ionic species from the atmosphere into the sample during poling was obtained from the growth of the infrared extinction peak associated with OH radicals. © 2006 American Institute of Physics.

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I. INTRODUCTION

Metallic clusters of nanometric size (hereafter called nanoparticles), either embedded in a host material or supported on a substrate, are increasingly used for a variety of applications involving the physics of surface plasmons.¹ Indeed, unique linear and nonlinear optical properties originate from the surface plasmon resonances of metallic clusters.² A great deal of interest arises from the capability of tailoring the resonances within a wide spectral range throughout the visible and near-infrared regions by the choice of the metal and host materials and by the manipulation of the size, shape, concentration, and spatial distribution of the nanoparticles.³

The recently discovered poling-assisted bleaching of

glass with embedded silver nanoparticles^{4,5} has renewed interest in thermal poling as a simple, reliable, and low-cost technique for controlling locally the surface-plasmon-resonant optical properties (such as absorption or refractive index) of metal-doped nanocomposite glasses.^{6,7} Thanks to this technique, large-area regular micro- and nanostructures have been demonstrated by modifying the spatial distribution of embedded nanoparticles, paving the route towards the realization of metallodielectric photonic crystals.⁷

The physical process responsible for poling-assisted bleaching has been identified at the earliest stage as the electric-field-assisted dissolution of embedded metallic clusters.^{4,5} The shape of the particles and their volume filling factor were found to have an influence on the bleaching.⁴ The dependencies of bleaching on poling conditions (temperature, voltage, and time) and the role of the glass-electrode contact have been studied as well.⁸ Physically, the dissolution of metallic clusters proceeds as follows.^{4,5} The internal electrostatic field which develops in the glass matrix

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underneath the anodic surface during poling causes the ionization of the clusters (assumed to be embedded in a thin near-surface layer facing the anode). As a result of cluster ionization, electrons are ejected from the clusters and extracted at the anode via tunneling from one cluster site to the nearest one; positively charged metallic ions are expelled from the clusters by strong Coulomb forces and migrate towards the cathode leaving behind them uncharged clusters. This process repeats itself until the clusters have been totally destroyed, i.e., *dissolved* in the glass matrix in the form of dispersed metallic ions. Note that the released metallic ions, provided that they possess sufficient mobility, could in turn participate to the ion migration process and therefore play a role in the formation of the internal electrostatic field. The particle shape is expected to have an influence on the dissolution process because ionization should be easier where the curvature of the cluster surface is higher (e.g., case of ellipsoidal particles) due to the stronger local electric field there. The filling factor of particle is also expected to have an influence on the dissolution process because of local field enhancement effects and reduction of the electron tunneling barrier as the average distance between particles decreases.

In this article, the emphasis is put on the influence of the volume filling factor of metallic clusters on poling-assisted bleaching. For this purpose we used commercially available samples made by standard float glass fabrication techniques, which contain spherical silver nanoparticles in a near-surface layer a few micrometers thick. Although the nanoparticle system in the samples did not present any particular three-dimensional spatial ordering (particles were randomly distributed in the host), it did exhibit a one-dimensional spatial dependence of particle concentration in the form of a decrease of the particle local volume filling factor across the depth.⁵ In fact, because the first stage of the fabrication process was an ion exchange between a $\text{AgNO}_3/\text{KNO}_3$ mixed melt and a soda-lime float glass, one ended up, after the Ag cluster aggregation stage, with a decreasing filling factor of Ag clusters across the depth. The existence of a filling factor depth profile complicates the analysis of experimental results but, as we will show it later, one can adapt the theoretical model used to describe the nanocomposite optical properties in order to include the (one-dimensional) spatial dependence of the filling factor. On the other hand, it is important to point out that one can take advantage of the filling factor depth profile for structuring the surface plasmon optical properties in the direction perpendicular to the sample surface, through either poling-assisted bleaching⁷ or femtosecond-laser-assisted deformation of particle shape.⁹ Hereafter we report on poling-assisted bleaching experiments on soda-lime silicate glasses containing spherical silver nanoparticles with different filling factor depth profiles. Optical extinction spectral measurements are used in order to quantify the bleaching, which can be observed macroscopically as a fading of the glass original color. Extinction spectra are modeled by the Maxwell Garnett effective medium theory¹⁰ which is adapted in order to take into account the filling factor depth profile. The position of the bleaching front (which delimits the region beneath the glass surface where clusters have been destroyed) is extracted from the

modeling and its dependencies on poling conditions are analyzed in order to determine the influence of the filling factor depth profile on bleaching.

The article is organized as follows. First the sample fabrication and characteristics are briefly described. In particular, a method is presented that allows us to determine the filling factor depth profile from measured extinction spectra. The theoretical expression of the optical extinction spectrum around the surface plasmon resonance is derived and the fitting procedure is validated in the case of etching experiments. Then the results of poling-assisted bleaching experiments are reported together with their analysis through fitting of extinction spectra. These results are interpreted in the light of the particle dissolution process. Finally conclusions are drawn and perspectives for further studies are pointed out.

II. SAMPLE FABRICATION AND CHARACTERISTICS

The samples used in our experiments were prepared from soda-lime float glass by $\text{Ag}^+ - \text{Na}^+$ ion exchange and subsequent annealing in a H_2 reducing atmosphere.¹¹ This fabrication method produced spherical silver nanoparticles of 30–40 nm mean diameter in a near-surface layer of a few microns thick. The volume filling factor of Ag nanoparticles ($f = V_{\text{Ag}}/V_{\text{Ag+glass}}$) peaked at the glass surface and decreased strongly within a few microns, as it was estimated through scanning electron microscope (SEM) analysis of the sample surface after successive etchings in HF acid.^{5,9} Sample's characteristics, both macroscopic (color) and nanoscopic (filling factor depth profile) ones, depended on detailed fabrication conditions and were different from batch to batch. The samples we used for our investigations were labeled according to batches from which they came from and were regrouped on the basis of optical extinction spectra (Fig. 1).

The determination of the filling factor depth profile by SEM analysis was time consuming. A theoretical modeling of the optical extinction spectrum including the one-dimensional spatial dependence of the filling factor could do the same job more easily. In principle, the filling factor depth profile could be determined by fitting the theoretical spectrum to the one measured on the pristine (fresh) sample. In practice, the surface plasmon resonance was so intense that the extinction measurement dynamic range was exceeded (i.e., transmitted light was below the detection level) over a large spectral range around the surface plasmon peak. As a result, measured spectra were truncated (see Figs. 1, 4, and 6) and the accuracy in the determination of the profile was reduced accordingly. In order to increase the accuracy, we performed the fitting on a set of extinction spectra which were measured on the same sample after removal of surface layers of various thickness by etching (as described in Ref. 9). The results obtained by this method will be discussed later (Sec. V). The filling factor depth profiles which were determined by fitting extinction spectra of fresh samples (27, 31, and 32) or etched samples (26, and 30) are shown in the inset of Fig. 1. The extinction spectra of samples 30 and 31 were almost identical, so that the inferred profiles were almost the same.

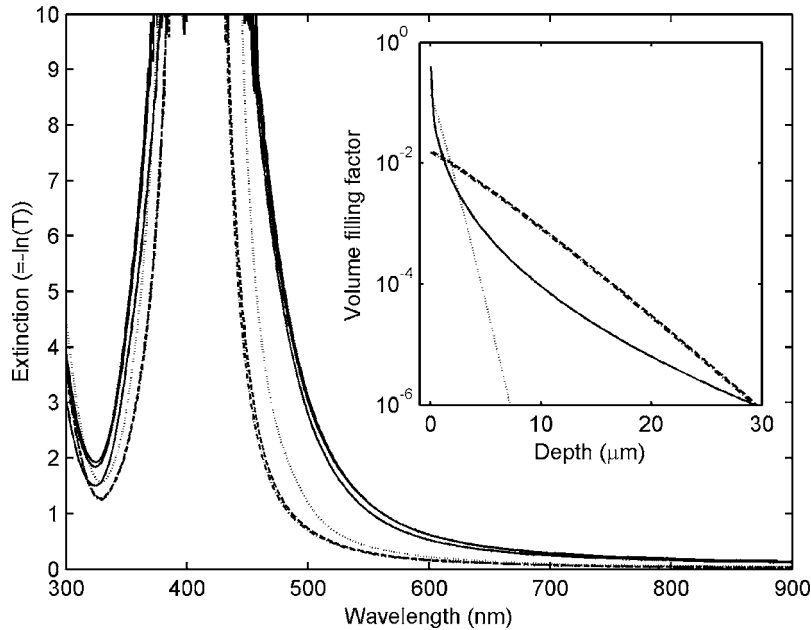


FIG. 1. Extinction spectra of silver-doped nanocomposite glass samples under test. Inset: volume filling factor of silver nanoparticles as a function of the depth under the surface (depth profiles were obtained by fitting extinction spectra to Eq. (1); values of profile parameters corresponding to best fits are listed in Table II). Samples: 25, 26, and 27 (solid lines), 30, and 31 (dashed-dotted lines), and 32 (dotted lines).

III. THEORETICAL EXTINCTION MODEL

Collective dipolar interactions between nanoparticles, which become more and more important as the average distance between particles decreases (i.e., as the volume filling factor increases), are well described by the Maxwell Garnett (MG) effective medium theory (see Ref. 12 for a critical discussion on MG modeling). This theory is valid as far as the wavelength of light is significantly longer than the particle dimensions and the average distance between particles, both conditions of which are verified in the case of our samples. The filling factor is defined as the volume of metallic inclusions per unit volume of composite material. For randomly distributed metallic nanoparticles, the filling factor may or may not be spatially constant in the nanocomposite. In our samples, the filling factor may be considered as constant in the transversal directions (y, z) parallel to the glass surface but not in the vertical direction (x) perpendicular to the surface.

In order to take into account the filling factor depth profile $f(x)$, we have adapted the Maxwell Garnett theoretical expression of the optical extinction (noted E) of the effective medium equivalent to the nanocomposite material,

$$E(\omega, d) = 2 \frac{\omega}{c} \int_d^L \sqrt{\frac{\varepsilon_i(\omega) + 2\varepsilon_h + 2 \times f(x) \times [\varepsilon_i(\omega) - \varepsilon_h]}{\varepsilon_i(\omega) + 2\varepsilon_h - f(x) \times [\varepsilon_i(\omega) - \varepsilon_h]}} dx, \quad (1)$$

where the expression under the square root is the effective dielectric constant ε_{eff} and the filling factor is expressed by an empirical function (the choice of such a function will be justified later),

$$f(x) = f_0 \exp[-(x/w_f)^\beta]. \quad (2)$$

In Eq. (1), c is the speed of light in the vacuum and ω is the angular frequency ($\omega = 2\pi c/\lambda$, λ : wavelength). The integral is performed from a distance d beneath the sample surface to a distance L that is equal to the sample thickness [in practice L can be chosen such that $f(x) \ll 1$ for $x > L$]. In fresh samples, d is taken equal to zero. In etched samples and bleached samples, d is different from zero and represents the etched thickness and the position of the bleaching front, respectively. In the expression of ε_{eff} , ε_h is the dielectric constant of the host medium (assumed here to be real and frequency independent) and ε_i is the complex and frequency-dependent dielectric constant of the metallic inclusions. In the frequency range of interest, $\varepsilon_i(\omega)$ is well approximated by the Drude model of metal,¹³

$$\varepsilon_i(\omega) = \varepsilon_b + 1 - \omega_p^2/(\omega^2 + i\omega\tau^{-1}), \quad (3)$$

where $\omega_p = e\sqrt{N/m\varepsilon_0}$ is the free electron plasma angular frequency (N : density of free electrons, m : effective electron mass, $-e$: electron charge, and ε_0 : permittivity of vacuum), ε_b is the contribution of core electrons to the dielectric constant of the metal, and τ is the collision time associated with collective electron excitations ($1/\tau$ represents the damping frequency of these oscillations). In the case of silver, $\hbar\omega_p = 9.2$ eV and $\varepsilon_i(\omega)$ is well approximated by taking $\varepsilon_b \sim 4$ and $\tau \sim 10$ fs.¹³ Empirically we found that adjustment of the value of τ from sample to sample was necessary in order to obtain good fitting of measured extinction spectra. In our calculations of the theoretical extinction [Eq. (1)], we took $L = 30 \mu\text{m}$, $\varepsilon_h = 2.2$, $\varepsilon_b = 3.9$, and τ in the range of 2–7 fs.

The theoretical evolution of extinction spectra of silver-doped nanocomposite glasses as a function of the parameter d is shown in Fig. 2 for two samples with different filling factor depth profiles. By varying d [the lower integration limit in Eq. (1)], one can simulate both etching and poling-assisted bleaching experiments and observe the influence of

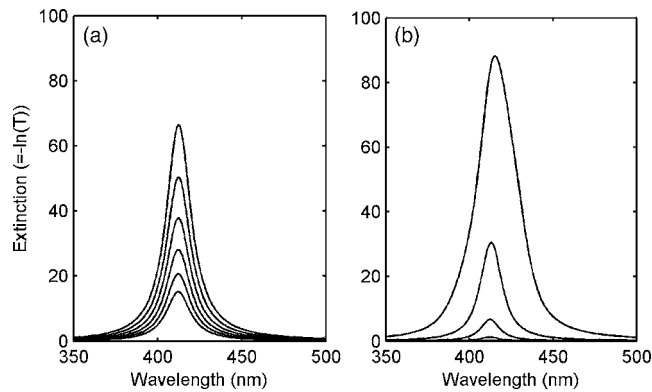


FIG. 2. Evolution of theoretical extinction spectra of silver-doped nanocomposite glasses with different filling factor depth profiles [(a) 31 and (b) 32] as layers of $1\ \mu\text{m}$ thickness are successively removed from the top surface (simulating, e.g., an etching experiment). Spectra are calculated using Eq. (1) with the parameters listed in Table II and $d=0, 1, 2, 3, 4$, and $5\ \mu\text{m}$. Spectra of decreasing intensities correspond to increasing values of d .

the filling factor depth profile on the results of these experiments. In the examples shown in Fig. 2, although both samples initially exhibit similar surface plasmon resonance strengths, a faster fading of the surface plasmon resonance with increasing d values is predicted for the sample which has higher near-surface values but steeper gradient of the filling factor.

IV. EXPERIMENTAL CONDITIONS

Thermal poling was carried out in air inside an oven using pressed-contact electrodes, with the silver-doped sample side facing the anode. Electrodes were made of hardened steel ($4 \times 5\ \text{mm}^2$), except for poling of sample 27 where polished silicon was used ($5 \times 5\ \text{mm}^2$). The thickness of all samples was equal to $1\ \text{mm}$. Thermal poling consisted in heating the sample up to a prescribed temperature, then applying the voltage for a certain time, and finally cooling the sample down to room temperature with the voltage still applied. In order to avoid runaway of poling current due to the high conductivity of soda-lime float glass, a modified poling procedure was used in previously reported experiments.⁴ In these experiments, the use of a relatively high poling temperature ($280\ ^\circ\text{C}$) required applying the voltage by small amplitude steps in order to safely reach a final voltage of $1\ \text{kV}$ or more.⁴ Such a modified procedure allowed us to bleach almost completely the surface-plasmon-resonant absorption in samples similar to the present ones.⁴ However, this procedure complicated the study of the bleaching dynamics due to the stepwise increase of the voltage during poling.⁸ Here, we decided to use moderately high poling temperatures (200 and $250\ ^\circ\text{C}$) which allowed us to apply the voltage at once and keep it constant during the whole poling duration (standard procedure). In order to avoid current runaway, however, the voltage had to be limited to about $1.5\ \text{kV}$. The incomplete bleaching of the samples (bleaching was proven to be more complete at higher temperatures and voltages⁸) was the price to pay for an easier interpretation of experimental results. Samples were poled at $200\ ^\circ\text{C}$ (27 and 30) or $250\ ^\circ\text{C}$ (31 and 32) with various poling voltages (from 0.5 to $1.5\ \text{kV}$) and for various times

(from 1 to $90\ \text{min}$). An ammeter (picoampere to milliampere range) in combination with a serial protection resistance ($100\ \text{k}\Omega$) was used for electrical current measurements.

Optical extinction spectra [$E = -\ln(I_{\text{out}}/I_{\text{in}})$, I : light intensity] were recorded over a broad spectral range (from 190 to $3300\ \text{nm}$) using UV-visible-infrared spectrometer (CARY 500) and a $2\ \text{mm}$ diameter aperture. The visible part of the spectrum was used to monitor the surface plasmon resonance of embedded silver nanoparticles whereas the near-infrared part was used to monitor the absorption of OH radicals (the latter was expected to increase due to injection of hydrogenated ionic species from the atmosphere during poling).

Etching experiments were performed by immersion of unprotected portions of the sample surface in diluted HF acid for various durations. The etched depth was monitored using a step surface profilometer.

V. EXPERIMENTAL RESULTS

A. Filling factor depth profiles

In the method we propose here for determining the filling factor depth profile, a set of wavelengths was first selected at which the extinction of the fresh sample did not exceed the measurement dynamic range. Then the evolution of the extinction as the sample surface was progressively etched was fitted for all the selected wavelengths simultaneously to the theoretical extinction [Eq. (1)] assuming an empirical mathematical expression for the filling factor depth profile [Eq. (2)]. Comparison was made between fittings with $\beta=1$ (exponential profile) and $\beta \neq 1$ (stretched exponential profile). In the latter case, parameters f_0 , w_f , and β in Eq. (2) and parameter τ in Eq. (3) were the only free parameters of the fitting. In the former case, we imposed $\beta=1$. Note that wavelengths on the UV side of the surface plasmon band were discarded because the shape of the extinction spectrum on that side was affected by the tails of absorption bands located at shorter wavelengths ($<300\ \text{nm}$). Results of the fitting are shown in Fig. 3 for samples 26 and 30. For sample 30 almost the same fitting quality was obtained with $\beta=1$ or $\beta \neq 1$ whereas for sample 26 good fitting could only be obtained with $\beta \neq 1$ (fitting parameters and quality are listed in Table I). These results pointed out the importance of an accurate description of the filling factor depth profile. The best fitting parameters are listed in Table II. Using these parameters, the corresponding extinction spectra were calculated by Eq. (1). These predicted spectra reproduced very well the experimental ones (Fig. 4), confirming the validity of the method.

Etching experiments were not performed on all samples. For the other samples (27, 31, and 32), the truncated extinction spectrum measured on the fresh sample was fitted to the theoretical spectrum [Eq. (1)] with $d=0$ and with f_0 , w_f , β , and τ as only free parameters (see spectra before poling in Fig. 6). The best fitting parameters are listed in Table II.

B. Poling-assisted bleaching

Poling-assisted bleaching could be observed qualitatively by the naked eye and using optical microscope

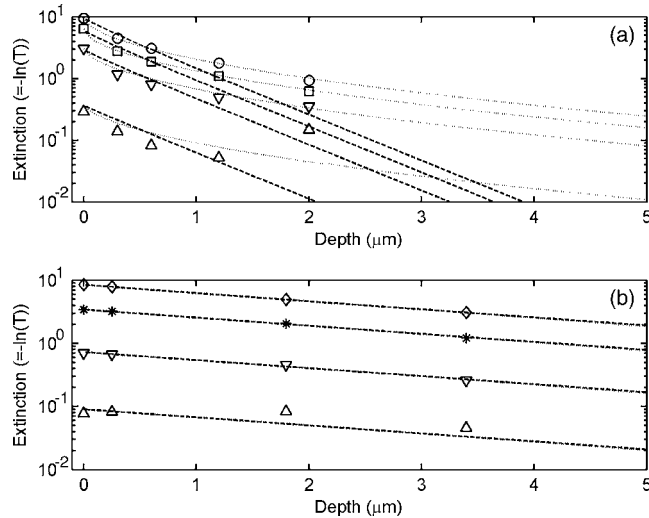


FIG. 3. Extinction of silver-doped nanocomposite glass samples at selected wavelengths (symbols) as a function of the etched depth. Samples: 26 (a) and 30 (b). Wavelengths: 435 nm (◇), 450 nm (*), 455 nm (○), 470 nm (□), 500 nm (▽), and 700 nm (△). Dashed lines and dotted lines are best fits to Eq. (1) assuming that the nanoparticle filling factor depth profile follows Eq. (2) with $\beta=1$ (exponential) and $\beta \neq 1$ (stretched exponential), respectively.

(Fig. 5). Quantitatively, it was evaluated by monitoring the surface-plasmon-resonant band (350–500 nm) after poling (Fig. 6). The peak of the surface-plasmon-band was found to be located at ~ 410 nm. The position of the bleaching front (indicated by vertical line in the insets of Fig. 6) was extracted from fitting of the extinction spectra. The extinction peak (not resolved in most samples!) was then calculated by substituting the extracted value of d into Eq. (1) and picking the peak of the surface-plasmon-resonant (SPR) band. Dependencies of both quantities on poling voltage and time were obtained (Fig. 7).

Comparing samples with very similar characteristics (30 and 31), bleaching turned out to be stronger (Fig. 5) when poling was carried out at 250 °C than at 200 °C, for identical poling voltages (1 kV) and times (60 min).

In the sample with the highest content of silver (27), strong bleaching was observed after poling at 200 °C, 1 kV for 60 min (Figs. 5 and 6). The bleaching was stronger than in a sample with lower silver content (30) which was poled in the same conditions (Fig. 5). This result was attributed partly to the higher filling factor (cf. Sec. VI) and partly to

TABLE II. Parameters obtained by fitting the extinction spectra of silver-doped nanocomposite glass samples assuming a stretched exponential depth profile of silver nanoparticles.

No.	f_0	w_f (μm)	β	τ (fs)
30	0.0148	3.820	1.11	5.2
31	0.0160	3.820	1.11	5.2
32	0.1349	0.760	1.10	6.7
25–27	0.4040	0.049	0.40	1.7

the better contact between the glass surface and the electrode, thanks to the use of polished silicon instead of steel as electrode material (actually, anodic bonding was observed after poling of sample 27 but the “stuck” electrode could be removed eventually after immersion of the sample into a liquid). The importance of tight glass-electrode contact for efficient bleaching was previously noticed and explained by the need to extract electrons ejected from the ionized silver clusters.⁸

In samples 31 and 32 poled under identical conditions (250 °C, 1 kV, and 60 min), the levels of bleaching were comparable (Figs. 5 and 6) although the bleaching front penetrated deeper in the depth of the former sample (Fig. 6, insets). A more quantitative comparison between samples 31 and 32 was provided by the dependencies of the bleaching front position on poling voltage and time, and the corresponding dependencies of the extinction peak (Fig. 7). The dependence of the bleaching front position on poling time provided us with interesting information on the poling-assisted bleaching dynamics and the influence of the filling factor on it (cf. Sec. VI). The bleaching front reached rapidly (after ~ 10 min) a steady-state position in sample 32 whereas it continued to penetrate slowly in the depth of sample 31 (at least up to ~ 90 min). Moreover, the bleaching front position increased less strongly with increasing poling voltage in sample 32 than in sample 31.

C. OH absorption monitoring

In a sample (25) poled at 280 °C up to 2.0 kV using the modified procedure (voltage increased by steps of 200 V, 10 min each step), the bleached area was found to extend beyond the electrode area (Fig. 8). A closer inspection revealed the presence of three bleaching zones: a yellowish outer ring, a colorless inner ring within the electrode area

TABLE I. Parameters obtained by fitting the extinction at selected wavelengths ($k=1, \dots, K$) as a function of etched depth ($i=1 \dots I$). The theoretical model is defined by Eqs. (1)–(3): f_0 , w_f and β determine the depth profile of the filling factor of silver clusters [Eq. (2)], and τ is the collision time associated with collective electron excitations within the silver clusters [Eq. (3)]. β was taken either as a free parameter or as a constant equal to 1 (these cases corresponded to either a stretched exponential or an exponential depth profile). The quantity to be minimized in fitting was: $\chi = \sqrt{\Psi/(I-1)}$, where $\Psi = \sum_k \sum_i (\delta_{i,k})^2$ and $\delta_{i,k} = E(\omega_k, d_i) - \tilde{E}(\omega_k, d_i)$ were the differences between measured and theoretical extinction values.

No.	f_0	w_f (μm)	β	τ (fs)	Ψ
30	0.0148	3.820	1.11	5.2	0.0224
	0.0159	3.434	1 (fixed)	5.2	0.0296
26	0.4040	0.049	0.40	1.7	0.1190
	0.1241	0.586	1 (fixed)	1.8	0.4128

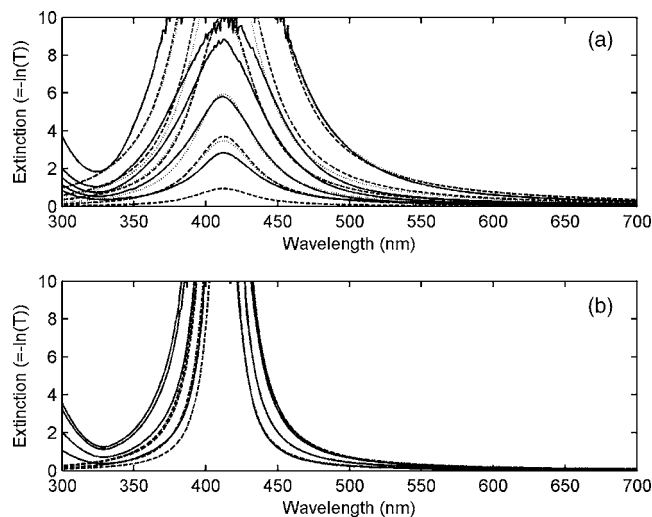


FIG. 4. Evolution of extinction spectra of silver-doped nanocomposite glass samples progressively etched from the top surface. Samples: 26 (a) and 30 (b). Solid lines are measurements. Dashed lines and dotted lines are predictions from Eq. (1) using parameters that were obtained by fitting the extinction at selected wavelengths as a function of etched depth (Fig. 3); they refer to fits obtained using either exponential or stretched exponential depth profile of the filling factor, respectively.

near the edges, and a colorless central area. The surface plasmon resonance band was measured in the three zones separately and decreased in the following order: outer ring, inner ring, and central area [Fig. 9(a)]. The near-infrared extinction peak associated with absorption by OH radicals, on the other hand, was almost unchanged in the central zone but increased in the inner and outer rings, being the highest in the inner ring [Fig. 9(b)]. This observation is a clear evidence of injection of hydrogenated ionic species from the atmosphere into the sample near the electrode edges and even under the electrode if small air gaps are present due to surface rough-

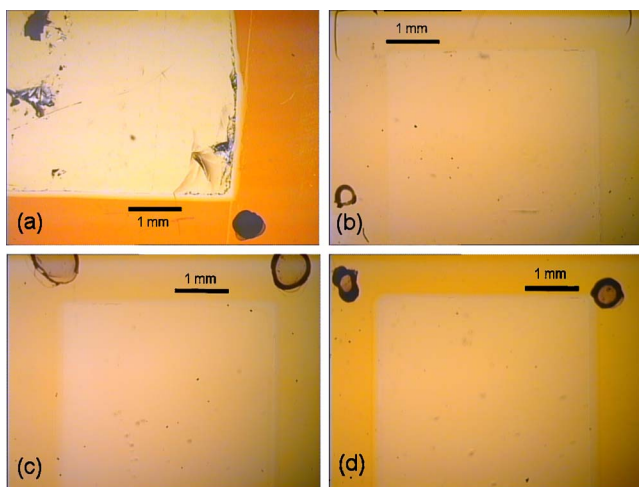


FIG. 5. (Color online) Optical microscope images (in transmission) of samples 27 (a), 30 (b), 31 (c), and 32 (d) after poling-assisted bleaching experiments. The original color of silver-doped nanocomposite glass ranged from dark orange to light orange according to the silver content. Bleached areas matched the electrode area (only a part of it is displayed). Poling voltage and time were equal to 1.0 kV and 60 min, respectively, for all samples. The poling temperature was equal to 200 °C [(a) and (b)] or 250 °C [(c) and (d)].

ness. Such a phenomenon is well known from poling experiments on silica glasses¹⁴ and it is observed here on metal-doped nanocomposite glasses.

The evolution of the sample's OH content, as determined from the measured extinction peak at ~ 2800 nm, is shown in Fig. 10 as a function of poling time and voltage for samples 31 and 32. The OH content increased both with poling time and poling voltage in the same way for both samples, indicating that the ion injection process did not depend on the nanocomposite characteristics and was essentially a "poling effect."

D. Poling current measurements

Decay of the poling current was observed during poling of silver-doped nanocomposite glass samples, as well as during poling of the original soda-lime silicate glass substrate (Fig. 11). In the case of the substrate, the current originated from thermally activated migration of ionic species (mainly Na^+ ions which are among the most mobile ionic species in glass in the temperature range of interest here). The current decayed with time because the blocking electrode condition¹⁵ was satisfied here (note that at higher temperatures and voltages, these conditions might be not satisfied anymore due to ion injection from the atmosphere). In the case of the nanocomposite samples, different types of charge carriers contributed to the current: Na^+ ions (present in the host material), Ag^+ ions, and electrons (released by the ionized Ag clusters). Sodium ions were likely to give the dominant contribution. The blocking electrode condition was satisfied both for the ions originally present in the host (Na^+) and for the continuously released ions (Ag^+) so that the total ionic current decayed with time. The electronic current, on the other hand, also decayed with time because the supply of released electrons (i.e. the ionized clusters) was eventually limited.

For identical poling conditions, sample thickness and electrode areas, the current was initially lower in the nanocomposites than in the substrate. A plausible explanation could be that the nanocomposite near-surface layer had a higher resistivity than the original glass because of the lower concentration of Na^+ ions (a certain amount of Na^+ ions was removed during the ion-exchange stage of the fabrication process).

VI. DISCUSSION

From the experimental and modeling results of samples 31 and 32, it is clear that the filling factor depth profile has an influence on poling-assisted bleaching. It is worth noting that a stretched exponential profile is required to model the extinction spectra of samples having a high filling factor near the surface ($f_0 > 0.1$). Physically, it could be an indication that the Maxwell Garnett description of the nanocomposite becomes inadequate at high filling factors.¹² According to our present understanding of the physics of the particle dissolution process, the penetration of the bleaching front in the depth is related to ion migration in the host material through the relation between ion depletion and local electrostatic field strength.

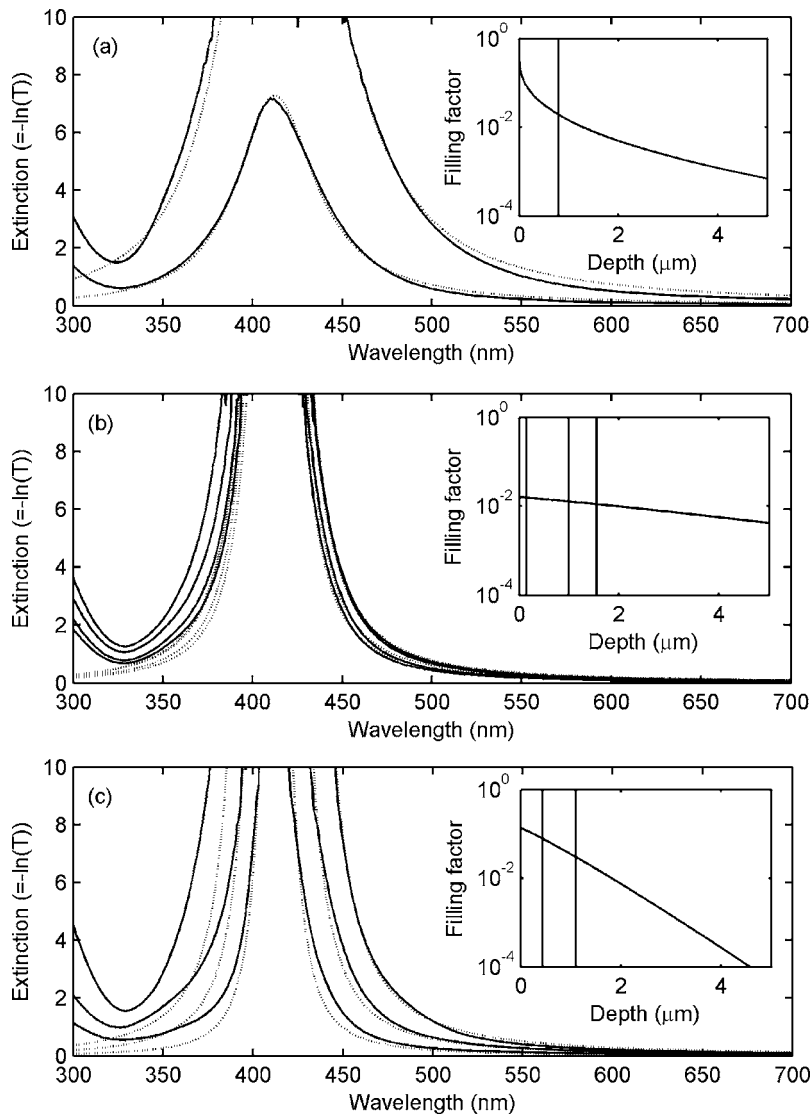


FIG. 6. Extinction spectra of silver-doped nanocomposite glass samples 27 (a), 31 (b), and 32 (c) measured before and after poling-assisted bleaching experiments (solid lines). Extinction spectra were fitted to Eq. (1) with the bleaching front position d as only free parameter (dotted lines). Values of fixed parameters are listed in Table II. Filling factor depth profiles are shown in the insets (vertical lines indicate the bleaching front position d after poling experiments). Poling conditions: 200 °C/1.0 kV/60 min (a), 250 °C/1.0 kV/5, 60, and 90 min (b) and 250 °C/1.0 kV/60 min and 250 °C/1.5 kV/60 min (c). For each experiment, the electrode was placed on a fresh area of the sample surface.

In a homogeneous glass, assuming the existence of a single ionic charge carrier and blocking electrodes, the ion depletion front moves in the depth with a time constant τ_{depl} given by¹⁶

$$\tau_{\text{depl}} = \frac{L}{\mu} \sqrt{\frac{\epsilon}{2eNV}}, \quad (4)$$

where μ and N are the mobility and the concentration of charge carriers, respectively, $-e$ is the electron charge, ϵ is the dielectric constant, L is the sample thickness, and V is the applied voltage. The ion depletion front eventually reaches a steady-state position at a depth d_{depl} given by¹⁶

$$d_{\text{depl}} = \sqrt{\frac{2\epsilon V}{eN}}. \quad (5)$$

In this model, it is assumed that the voltage is applied at once and maintained constant during the whole duration of poling. Strictly speaking, the model would not be applicable to describe previous poling experiments⁴⁻⁸ where the voltage was applied step by step. This remark justifies our choice to operate at lower poling temperatures in order to be able to apply the voltage at once (cf. Sec. IV).

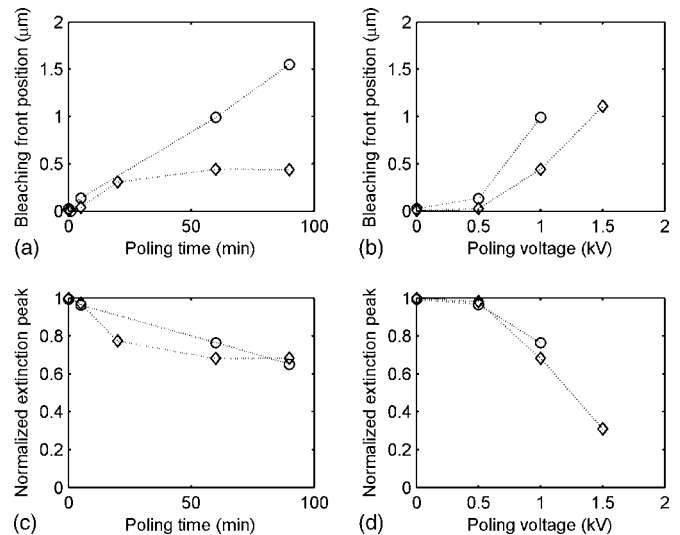


FIG. 7. Bleaching front position [(a) and (b)] and normalized extinction peak [(c) and (d)] as a function of poling time [(a) and (c)] and poling voltage [(b) and (d)] in samples 31 (○) and 32 (◇). The bleaching front position d was obtained by fitting the extinction spectra of poled samples (Fig. 5). The normalized extinction peak was defined as $E(\omega_p, d)/E(\omega_p, d=0)$ where the extinction was calculated using Eq. (1) at the surface plasmon resonance frequency ($\lambda_p \sim 410$ nm). Poling conditions: 250 °C, [(a)–(d)], 1.0 kV [(a) and (c)], and 60 min [(b) and (d)].

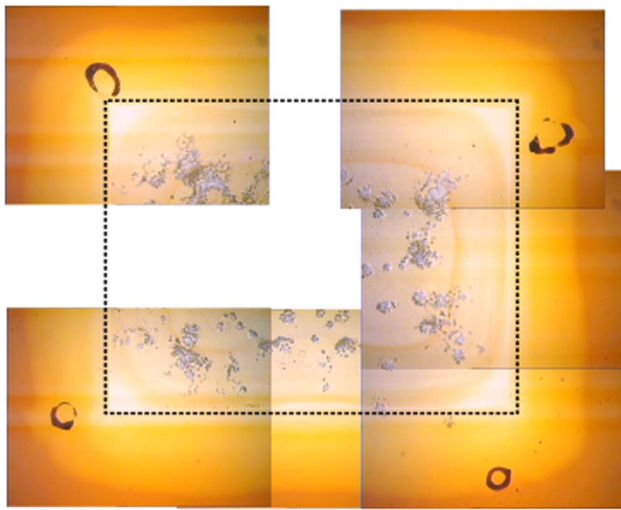


FIG. 8. (Color online) Optical microscope image (in transmission) of silver-doped nanocomposite glass sample (25) after a poling-assisted bleaching experiment at 280 °C with the voltage increased by steps of 0.2 kV (10 min each step) up to 2.0 kV. The electrode area (6×9 mm²) is represented by a dotted rectangle. Three zones can be distinguished: a yellowish outer ring outside the electrode area, an inner ring inside the electrode area near the edges, and a central zone where the sample color (originally orange) has faded away.

In our silver-doped nanocomposite glasses, the ion depletion process is more complicated than the one described by this simple single carrier model. Firstly, in the nanocomposite near-surface layer, the ionic conductivity is expected to be lower than in the original glass. Indeed, at the stage of the nanocomposite fabrication process, Na⁺ ions were removed from the near-surface layer by Na⁺–Ag⁺ ion exchange and Ag⁺ ions were then aggregated to form Ag clusters. The higher the filling factor of Ag clusters, the lower the Na⁺ concentration and the lower the ionic conductivity of the nanocomposite layer. This situation should remain valid during poling as far as the dissolution of clusters is only begin-

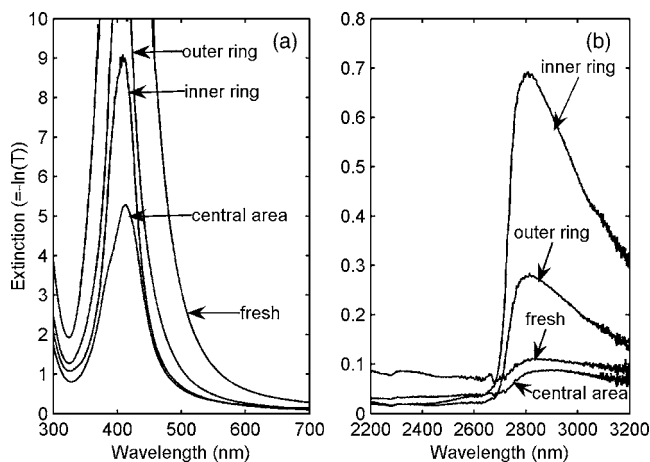


FIG. 9. Extinction spectra of silver-doped nanocomposite glass sample (25) measured over a broad spectral range after a poling-assisted bleaching experiment at 280 °C with the voltage increased by steps of 0.2 kV (10 min each step) up to 2.0 kV. Spectral ranges of the surface plasmon resonance and of the absorption by OH radicals are shown in separate charts [(a) and (b), respectively]. Spectra were recorded through a 2 mm diameter aperture located at different positions on the sample surface (see Fig. 8).

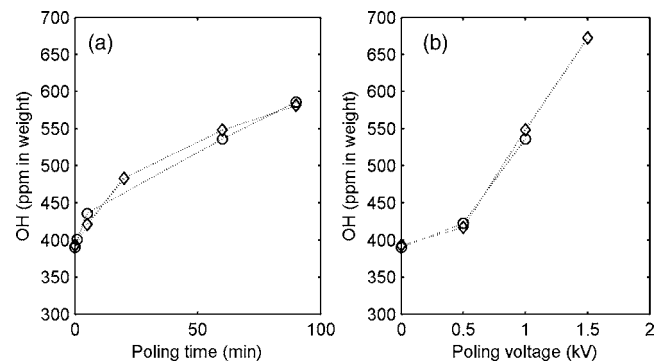


FIG. 10. OH content as a function of poling time (a) and poling voltage (b) in samples 31 (○) and 32 (◇). Poling conditions: 250 °C [(a) and (b)], 1.0 kV (a), and 60 min (b). The weight percentage in OH was calculated by $w_{OH}(\%) = 0.1 \times \alpha_{OH} / \varepsilon_{OH} \times M_{OH} / \rho$, where α_{OH} is the OH absorption coefficient [$\alpha_{OH} = E_{OH} / (l \ln(10))$], l is the sample thickness, and E_{OH} is the sample extinction measured around 2.8 μm , $\varepsilon_{OH} = 50 \text{ l/mol cm}$ and M_{OH} is the OH molar weight.

ning. It appeared to be the case during the first 20 min of poling at 250 °C and 1 kV where the poling current decayed slower in the nanocomposites than in the original glass (Fig. 10). Secondly, as Ag clusters start to be ionized by the electrostatic field which develops underneath the anodic surface, the release of both Ag⁺ ions and electrons increases the electrical conductivity of the nanocomposite glass. As far as they possess similar mobility as Na⁺ ions, the released Ag⁺ ions have a direct impact on the ionic conductivity, which can be crudely estimated in the frame of the single carrier model assuming $\mu_{Ag^+} \cong \mu_{Na^+}$ and $N = N_{Ag^+} + N_{Na^+}$. The higher the filling factor of Ag clusters, the higher the concentration of released Ag⁺, the shorter the ion depletion time constant [Eq. (4)], the smaller the ion depletion steady-state depth [Eq. (5)]. The faster penetration and the smaller steady-state depth of the bleaching front which were observed in sample with higher filling factor in near-surface layers (Fig. 7) are consistent with this prediction and show that ion migration process and bleaching process are closely related. Moreover, on the basis of the same arguments, the higher the filling factor, the less strong the increase of the ion depletion steady-state depth with increasing voltage [Eq. (5)]. This trend was indeed observed in the dependence of the bleach-

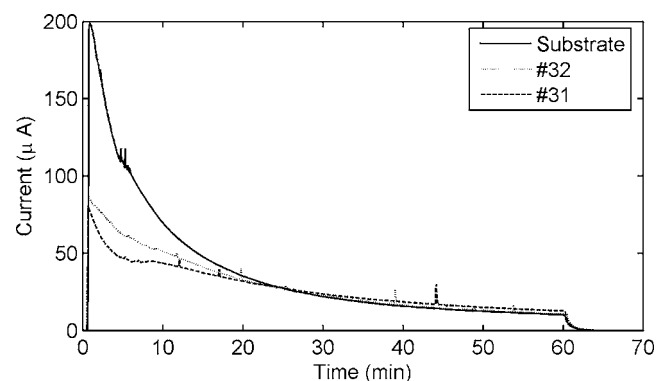


FIG. 11. Evolution of the current during poling of silver-doped nanocomposite glass samples (31 and 32) and original soda-lime glass substrate. Poling conditions: 250 °C and 1 kV.

ing front on poling voltage: the bleaching front increases less rapidly in sample with higher filling factor (Fig. 7).

Electronic conductivity plays an important role in poling-assisted bleaching. However, the different natures of conduction mechanisms for electrons and ions do not allow us to tackle the role of released electrons in the same way as for released Ag^+ . Released electrons eventually reach the anode by tunneling from one cluster site to the nearest one. The higher the filling factor of Ag clusters, the lower the height of the tunneling barrier.⁵ Moreover, the presence of interstitial cations is expected to cause a further reduction of the tunneling barrier.⁵ In summary, the electronic conductivity is expected to play an increasing role in regions where the filling factor increases (towards the glass surface in all our samples).

Finally, injection of hydrogenated ionic species (H^+ , H_3O^+) from the atmosphere into the sample (around the anode or even under it due to surface roughness) was shown to affect poling-assisted bleaching in some circumstances (Figs. 8 and 9). On one hand, as soon as they reach the glass surface, H^+ or H_3O^+ ions can help to neutralize electrons released by the dissolution process, effectively playing the role of an “electrode.” This first effect is believed to explain the partial bleaching of the sample *outside* the electrode area [Figs. 8 and 9(a)]. On the other hand, penetration of H^+ or H_3O^+ ions underneath the electrode is known to modify the ion-depletion process through partial neutralization of the space charge, leading to a decrease of the internal dc field strength.¹⁴ This second effect is believed to explain the reduced bleaching in the inner ring (inside the electrode area near its edges) as compared to the central region [Figs. 8 and 9(a)].

VII. CONCLUSIONS

Poling-assisted bleaching experiments were carried out on soda-lime float glasses containing spherical silver nanoparticles with a decreasing filling factor across the depth. Samples with different filling factor depth profiles were compared. Maxwell Garnett effective medium theory was adapted in order to take into account the filling factor depth profile in the calculation of the optical extinction spectrum. Modeling of measured extinction spectra allowed us to reveal the dependencies of the bleaching front position on poling time and voltage and to gain access to the corresponding dependencies of the surface plasmon peak. Evidence of injection of hydrogenated ionic species from the atmosphere

into the sample during poling was obtained. This effect is believed to influence poling-assisted bleaching through modification of ion depletion in near-surface layers and electron neutralization at the anodic surface. Further studies are needed to verify these statements. Experimental and modeling results were found to be consistent with our present understanding of the electric-field-assisted dissolution process and brought insight on the influence of the volume filling factor of metallic clusters. In particular, it was confirmed that bleaching proceeded faster and easier in regions of higher filling factor.

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